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METHOD FOR MANUFACTURING NYLON 6

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### Claims

1. A method for manufacturing nylon 6 which consists of a polymerization process in which a nylon 6 monomer is polymerized at or above its melting point in the presence of a silicate and a cooling process in which the temperature of said nylon 6 is lowered from said level at or above the melting point to 160°C or below at a controlled cooling rate.

2. The method for manufacturing nylon 6 specified in Claim 1 in which the temperature of nylon 6 is lowered from said level at or above the melting point to 160°C or below at a cooling rate of 4°C/min or below in said cooling process in order to manufacture a nylon 6 characterized by an  $\alpha$ -type crystalline structure.

3. The method for manufacturing nylon 6 specified in Claim 1 in which the temperature of nylon 6 is lowered from said level at or above the melting point to 160°C or below at a cooling rate of 10°C/min or above in said cooling process in order to manufacture a nylon 6 characterized by a  $\gamma$ -type crystalline structure.

#### Detailed explanation of the invention

#### Industrial application fields of the invention

The present invention concerns a method for manufacturing nylon 6 of any desired crystalline structure (i.e.,  $\alpha$ -type or  $\gamma$ -type).

#### Precedent techniques of the invention

Nylon 6 is praised as a representative engineering plastic since it exhibits well-balanced properties. In particular, it is expected that the demand for said polymer will continuously increase among auto manufacturers in the future.

Since nylon 6 is a crystalline polymer, it exhibits excellent tensile strength and rigidity. Due to said crystallinity, however, the impact strength is less than satisfactory when said polymer is used for automotive exterior

panels, etc. In particular, it has been reported that the impact strength of a nylon 6 manufactured by the accelerated alkali catalyst polymerization method, which is suitable for large components, is lower than that of a nylon 6 manufactured by the hydrolytic polymerization method (see M. I. Kohan, Nylon Plastics (Interscience, 1973), p. 457).

The improvement of the impact strength of nylon 6 is one of the most important technical objectives in the nylon industry. Attempts have been made to improve the impact strength by blending or copolymerizing an elastomer (e.g., see Japanese Kokoku Patents Nos. Sho 61[1986]-3809 and Sho 54[1979]-40120). If these methods are implemented, however, a noncrystalline or low-crystallinity nylon 6 is inevitably produced.

The crystalline structure of nylon 6 may be the  $\alpha$ -type, which is a planar zigzag structure, or the  $\gamma$ -type, which is a spiral structure. The  $\alpha$ -type nylon 6 has a high melting point and a high density, whereas the  $\gamma$ -type nylon 6 has a low melting point and a low density. This type exhibits intermediate properties between the  $\alpha$ -type and the noncrystalline type.

The  $\alpha$ -type nylon 6 is better for a component which requires a higher rigidity, whereas the  $\gamma$ -type is more desirable for a component which requires a higher impact strength. Then the effectiveness of nylon 6 is maximized. For this reason, it has become urgent to selectively manufacture an  $\alpha$ -type or  $\gamma$ -type nylon 6.

Only the stable type (i.e.,  $\alpha$ -type) nylon 6 is obtained in the conventional method. The  $\gamma$ -type is obtained only by a special treatment (e.g., iodine treatment of the  $\alpha$ -type, etc.)

(see L. E. Alexander, "X-ray diffraction of polymers," Kagaku Dojin, 1973).

The present inventors compiled exhaustive research in order to solve the aforementioned problems. Thus, the present invention has been completed.

#### Objectives of the invention

The present invention provides a simple method for selectively manufacturing a nylon 6 with  $\alpha$ -type or  $\gamma$ -type crystalline structure.

#### Composition of the invention

Put succinctly, the present invention concerns a method for manufacturing nylon 6 which consists of a polymerization process in which a nylon 6 monomer is polymerized at or above its melting point in the presence of a silicate and a cooling process in which the temperature of said nylon 6 is lowered from said level at or above the melting point to 160°C or below at a controlled cooling rate.

Next, the composition of the present invention will be explained in further detail.

When the concept of the present invention is actualized, polymerization is induced in the presence of a silicate, and the cooling rate is controlled during a cooling process. As a result, a nylon 6 with an  $\alpha$ -type or  $\gamma$ -type crystalline structure is selectively manufactured.

Concrete examples of silicates include montmorillonite, vermiculite, halloysite, etc. These silicates may be used either alone or in combinations of two or more.

Said silicate should be first swollen by an organic compound so that said silicate will be homogeneously dispersed in the nylon 6 monomer. There are no special restrictions on the types of said organic compounds so long as they exert no adverse effects on the polymerization process. Thus, hydrocarbons, amines, carboxylic acids, alcohols, halogenated compounds, etc., can be used. In particular, compounds which contain intramolecular onium ions which form strong chemical bonds by a cation-exchange reaction with a silicate are especially desirable. Concrete examples of such organic compounds include high-acidity salts of trimethylamine, triethylamine, hexylamine, cyclohexylamine, dodecylamine, ethylenediamine, hexamethylenediamine, hexamethylenetetramine, polyallylamine, pyridine, aniline, benzylamine, bis(aminomethyl)benzene, aminophenol, alanine, 4-aminobutyric acid, 6-aminocaproic acid, 12-aminododecanic acid, 16-aminohexadecanic acid, etc. It should be noted, however, that the aforementioned examples in no way constitute an exhaustive list. As "high-acidity" compounds, hydrochloric acid, hydrobromic acid, sulfuric acid, phosphoric acid, etc., can be used. The aforementioned organic compounds may be used either alone or in combinations of two or more.

The quantity of the aforementioned silicate (during the polymerization process) with respect to 100 parts by weight of the nylon 6 monomer should be 0.001-100 parts by weight. If the quantity of addition is smaller than 0.001 parts by weight, a mixture of the  $\alpha$ -type and  $\gamma$ -type tends to be produced. If the

quantity of addition exceeds 100 parts by weight, a high-viscosity reaction mixture is produced. Thus, the reaction rate tends to stagnate. Especially desirable results are obtained if the quantity of addition is kept at 0.01-50 parts by weight.

When nylon 6 is polymerized, conventionally known techniques (e.g., method for hydrolyzing caprolactam, method for polymerizing caprolactam in the presence of an alkali catalyst, method for dehydrating and polymerizing 6-aminocaproic acid, etc.) can be appropriately used.

The polymerization temperature must be at or above the melting point of nylon 6. Generally speaking, the melting point of said polymer is approximately 220°C. If the polymerization temperature is lower than the melting point of nylon 6, crystals are deposited during the polymerization process. Thus, it is impossible to deposit crystals by controlling the cooling rate, which is the main objective of the present invention.

Concrete examples of nylon 6 monomers include caprolactam, 6-aminocaproic acid, etc. These monomers may be used either alone or in combinations of two or more.

Additives which exert no substantial adverse effects on the polymerization process (e.g., glass fiber, pigments, antioxidants, etc.) may be present during the polymerization process.

The temperature of the resulting polymerized nylon 6 is lowered from the aforementioned level at or above the melting point to 160°C or below in the subsequent cooling process. If the cooling rate is regulated in the present process, a nylon 6 with the  $\alpha$ -type or  $\gamma$ -type crystalline structure is obtained. If the control of the cooling rate is stopped before the temperature

drops to 160°C, it is impossible to produce a nylon 6 with the objective crystalline structure.

When an  $\alpha$ -type nylon 6 is manufactured, the cooling rate must be 4°C/min or below. When a  $\gamma$ -type nylon 6 is manufactured, on the other hand, the cooling rate must be 10°C/min or above.

In other words, if the cooling rate is 4°C/min or below, at least 90% of the resulting nylon 6 has  $\alpha$ -type crystalline structure. Then the cooling rate should be at least 0.1°C/min. If the cooling rate is lower than 0.1°C/min, the overall cooling period exceeds 24 h, which is disadvantageous for industry. Concrete examples of cooling methods include a method in which a reaction container in which nylon 6 has been polymerized is immersed in an oil bath after the polymerization process so that the temperature will be lowered due to the spontaneous heat release of said oil, etc. The temperature, furthermore, may be gradually lowered by precisely programming the cooling process.

If the cooling rate is above 10°C/min, at least 90% of the resulting nylon 6 has  $\gamma$ -type crystalline structure. Then the cooling rate should be no higher than 900°C/min from a practical point of view. Concrete examples of cooling methods include a method in which a reaction container in which nylon 6 has been polymerized is removed from a heating device (e.g., oil bath, etc.) after the polymerization process has been completed and (A) in which said reaction container is cooled with air at room temperature, (B) in which said reaction container is externally cooled by ice water, (C) in which said reaction container is externally cooled by liquid nitrogen, or (D) in which a molten nylon 6 is added to water. The temperature, furthermore, may be quickly lowered by precisely programming the cooling process.



The nylon 6 product obtained in the method of the present invention may be a composite of nylon 6 and a silicate depending on the quantity of the silicate added. As the present inventors noted earlier (see Japanese Patent Application No. Sho 60[1985]-217396), said composite exhibits excellent mechanical strength and heat resistance since the nylon 6 and silicate have been bonded molecularly. Thus, said composite can be effectively used. Silicates can be selectively removed from said composite by dissolving nylon 6 in an appropriate solvent (e.g., m-cresol, formic acid, m-cresol/chloroform mixture, etc.).

#### Effects of the invention

If the concept of the present invention is actualized, a nylon 6 with  $\alpha$ -type or  $\gamma$ -type crystalline structure can be manufactured with simple procedures. The exact functional mechanism by which the aforementioned effects of the present invention are obtained has yet to be clarified, but these effects may be safely attributed to the presence of a silicate during the polymerization process and the controlled cooling rate in the cooling process of the present invention.

#### Application examples

The contents of the present invention will be explained below in further detail with reference to application examples.

Application Example 1

After 100 g of montmorillonite ("Cunipia F [transliteration]," trademark of Cunimine Kogyo [transliteration] Co.) had been dispersed in 10 L of water, 51.2 g of 12-aminododecanic acid and 24 mL of concentrate hydrochloric acid were added to the resulting dispersion. After the contents had been agitated over a 5-min period, the resulting mixture was filtered. After said mixture had been sufficiently washed, it was dried in a vacuum. As a result, a montmorillonite swollen by the hydrochloride of 12-aminododecanic acid ("12-M" below) was obtained.

After 100 g of caprolactam and 0.2 g of the aforementioned 12-M had been put in a reaction container equipped with an agitation mechanism, the contents were agitated in an oil bath at 100°C. As a result, a homogeneous high-viscosity dispersion was obtained. After 2.4 g of sodium hydride had been added to said dispersion, the temperature of the resulting mixture was raised to 250°C in an oil bath. After 1.37 g of N-acetylcaprolactam had subsequently been added, the contents were continuously heated for an additional 30 min. Subsequently, the reaction container was removed from the oil bath and then externally cooled with ice water. The temperature was lowered to 100°C at 40-20°C/min.

After the resulting nylon 6 had been pulverized, the planar gap (d) was measured by X-ray diffraction using  $\text{CoK}\alpha$  rays. As a result, a peak attributed to the  $\gamma$ -type was observed at 4.2 Å, whereas no peaks attributed to the  $\alpha$ -type (i.e., peaks at 4.4 Å and 3.8 Å) were observed. Thus, the aforementioned polymer had a virtual  $\gamma$ -type structure.

### Application Example 2

Polymerization procedures identical to those in Application Example 1 were carried out. After nylon 6 had been polymerized, the heating process was halted. Then the temperature of the reaction container was gradually lowered in an oil bath. More specifically, the temperature was gradually lowered to 100°C at 2.8-0.5°C/min.

When the planar gap (d) of the resulting nylon 6 was measured according to procedures identical to those in Application Example 1, peaks were observed at 4.4 Å and 3.8 Å, but no peak was observed at 4.2 Å. Thus, the aforementioned polymer had a virtual  $\alpha$ -type structure.

### Comparative Example 1

Polymerization procedures identical to those in Application Example 1 were carried out except that the reaction container was heated using a mantle heater connected to a programmed temperature controller. Subsequently, the temperature of the resulting polymer was lowered to 100°C at a cooling rate of 5°C/min.

When the planar gap (d) of the resulting nylon 6 was measured according to procedures identical to those in Application Example 1, peaks of comparable intensities were observed at 4.4 Å, 4.2 Å, and 3.8 Å. When the peak area ratio of the respective crystalline types was computed, it was determined that the  $\alpha$ -type: $\gamma$ -type ratio of the aforementioned nylon 6 was 60:40.

### Comparative Example 2

Nylon 6 polymerization procedures and cooling procedures identical to those in Application Example 1 were carried out except that 12-M used in Application Example 1 was dispensed with. Then the planar gap (d) was measured.

As a result, no peaks were observed at 4.4 Å and 3.8 Å, whereas a peak was observed at 4.2 Å. Thus, the aforementioned polymer nylon 6 had a virtual  $\alpha$ -type crystalline structure.

The measurement data obtained in Application Examples 1 and 2 and Comparative Examples 1 and 2 are summarized in the table.

As the results of the table clearly indicate, a nylon 6 of any desired crystalline structure (i.e.,  $\alpha$ -type or  $\gamma$ -type) is obtained in each application example.

	1	2	3
	12-M (重量部)	冷却速度 (°C/分)	結晶構造 (型)
実施例 1	0.2	40~20	$\gamma$
" 2	0.2	25~0.5	$\alpha$
比較例 5 1	0.2	5.0	$\alpha + \gamma$
" 2	0	40~20	$\alpha$

- Key: (1) 12-M (parts by weight)  
 (2) Cooling rate (°C/min)  
 (3) Crystalline structure (type)  
 (4) Application Example  
 (5) Comparative Example